

Some Thermodynamic Properties of Bromobenzene from 0 to 1500 K*

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(June 17, 1975)

Measurements were made of the heat capacity of crystalline and liquid bromobenzene from 11 to 300 K, of the triple point and heat of fusion at the triple point and of the heat of vaporization at one temperature. The adiabatic calorimeter used was precise over most of its range to ± 0.1 percent; the purity of the sample was 99.998 mol percent. The triple point of pure bromobenzene is 242.401 K (-30.749°C) $\pm 0.010^\circ$; the enthalpy and entropy of fusion are, respectively, $10702 \pm 5 \text{ J mol}^{-1}$ and $44.150 \pm 0.022 \text{ J K}^{-1} \text{ mol}^{-1}$. The heat and entropy of vaporization at 293.00 K are, respectively, $43\,963 \pm 60 \text{ J mol}^{-1}$ and $150.0 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$. Tables are given for the thermodynamic functions of the condensed phases from 0 to 300 K; the functions for the ideal gas from 100 to 1500 K, calculated from spectroscopic and molecular data using statistical mechanical methods, are also tabulated. The entropy of the ideal gas at 293.00 K and one atmosphere, from statistical mechanics, is $323.63 \text{ J K}^{-1} \text{ mol}^{-1}$; the same quantity from the experimental measurements (third law) is $323.73 \text{ J K}^{-1} \text{ mol}^{-1}$. No anomalies or additional transitions were observed.

Key words: Bromobenzene; calorimetry; enthalpy; entropy; Gibbs energy; heat capacity; heat of fusion; heat of vaporization; thermodynamic properties, triple point.

1. Introduction

The experimental work reported in this paper was carried out at the National Bureau of Standards in 1945, as part of a program supported by the Office of Rubber Reserve. The calculations of results were not completed, and the work was never reported, both because of the pressure of more urgent research, and because the desired inclusion of ideal-gas properties was not possible with the incomplete and controversial molecular data available at that time.

Although the literature on the physical and molecular properties of bromobenzene is voluminous, there has been reported only one set of heat capacity measurements [1]¹ over a wide range of temperature. Since these extended no lower than 90 K, and were performed by a method which is inherently less accurate than the adiabatic calorimeter, it was thought desirable to make a complete set of measurements of thermal properties of the condensed phases of bromobenzene from room temperature down to near 11 K, these limits being imposed by the precise adiabatic calorimetry apparatus then available.

Measurements were made of the heat capacity of solid and liquid bromobenzene, the triple point, the heat of fusion at the triple point, and the latent heat of vaporization at one temperature (293 K). Recently these measurements have been smoothed, adjusted to

more modern units and scales, and combined with a new calculation of ideal-gas properties to create the consistent set of thermodynamic properties presented here.

2. Experimental Detail

2.1. Calorimetric Apparatus

The identical calorimetric apparatus described in great detail by Scott, Meyers, Rands, Brickwedde, and Bekkedahl [2] was used for all the measurements on bromobenzene. Only a brief resumé need be given here. The copper sample container (the calorimeter proper), with its heater and calibrated platinum resistance thermometer, was suspended by a long, vertical, rigid Monel tube from a valve exposed to ambient conditions. Thus the calorimeter could be evacuated and samples could be introduced and removed by vaporization without disturbing the assembly. The copper radiation shield surrounding the calorimeter had three separate control heaters on its surface, and two more were used for the tube above the calorimeter and for the bundle of electrical leads. A brass can, connected to a high-vacuum system, enclosed the calorimeter and shield. This can was in turn immersed in a Dewar which contained appropriate coolants or baths for the various temperature regions investigated. For the lowest temperature region, a multiple Dewar system was used. The inner Dewar was filled with liquid hydrogen, and the pressure above it was reduced by a high-capacity pump to less

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¹ Figures in brackets indicate literature references at the end of this paper.

than that of the triple point of hydrogen. An outer Dewar contained liquid air at ambient pressure.

The whole apparatus was designed for rapid temperature equilibration within the calorimeter, rapid response in the manual adiabatic control system, nearly complete thermal isolation of the calorimeter from its surroundings, and precision and accuracy in the measurement of temperature and electrical energy. The temperatures were determined to a precision of one millidegree over most of the range; time intervals were recorded with an accuracy of one hundredth of a second; and the voltage and current of the steady DC power supply were measured to one-tenth millivolt and one microampere, respectively. The various electrical instruments had been recently calibrated by the Electricity Division of the National Bureau of Standards. Details may be obtained by consulting reference [2].

2.2. Sample

A quantity of distilled bromobenzene was furnished through the kindness of Dr. D. R. Stull of the Dow Chemical Company. About one liter of this material was redistilled at atmospheric pressure using a column 75 cm long packed with stainless steel helices and fitted at the head with a platinum resistance thermometer. The change of temperature during the distillation followed closely the change in barometric pressure, giving no indication of fractionation; nevertheless, only the middle third of the distillate was used for further purification. The latter was accomplished by four successive freezings and meltings in vacuum; the portions of material (20–30 ml) which remained unfrozen or were the first to melt, each time, were discarded without breaking the vacuum. The remaining 75 ml (approximately) of purified material were transferred to a clean, evacuated weighing container and subsequently vaporized into the evacuated calorimeter vessel. The mass of the sample was 104.4904 g.

The purity of the sample is discussed below (sec. 2.4) in connection with the triple-point measurements. It was so high that chemical analyses could have added no useful information, and none were made.

2.3. Heat Capacity

Measurements of the heat capacity of the calorimeter plus sample were carried out in the usual manner by obtaining ratios of measured increments of added electrical energy to the resulting temperature increments. The temperature increments used were of the order of ten degrees over most of the range and as low as two degrees in the region below 30 K.

A total of 89 observations of $\Delta Q/\Delta T$, in eleven "runs," were made. These were corrected to dQ/dT by the method of Osborne, Stimson, Sligh, and Cragoe [3] wherever necessary; the maximum correction was 0.3 percent for two measurements at very low temperature, with most corrections amounting to less than a few hundredths percent. All of the energy values have been converted from the "international" units, in which the measuring instruments were calibrated, to the presently used (absolute) joule (1 international joule =

1.000165 (absolute) joules); likewise, mean temperatures were changed slightly to correspond with the International Practical Temperature Scale of 1948 [4] above 90 K, and to the NBS-1955 provisional scale (numerically 0.01° lower than the NBS-1939 scale [5]) below 90 K. Other possible corrections, such as for impurities or for pre-melting of the solid, were calculated to be negligible.

The differences between the observed values of $C = dQ/dT$ and values calculated from empirical functions of temperature (two for solid bromobenzene, overlapping in the region of 35 K, and one for the liquid) were plotted on large scale and smooth curves drawn through them. From these functions and the corresponding difference curves, tables of C at closely spaced equal temperature intervals were constructed, then smoothed by a 9-point smoothing formula [6]. The deviations of the observed values from the smoothed table are plotted against the mean temperatures of the observations in figure 1. In the figure, lines are used to connect the observations within a run. It is seen that, with the exception of three inexplicably low values, the measurements are precise to about 0.1 percent or better.

A normal procedure would have been to make measurements also of the heat capacity of the calorimeter containing a very small quantity of bromobenzene, over the entire temperature range, so that the two sets of measurements could be subtracted with little or no correction for vapor. This procedure was not followed because time could be saved by using an already smooth and accurate table of heat capacities of the completely empty calorimeter from 90 to 300 K [7], and because it was estimated that the vapor correction would be extremely small and amenable to precise calculation. Therefore, after all sample had been removed, heat capacity measurements were made on the calorimeter itself from 14 to 95 K. After corrections were made for curvature and for a few torr pressure of helium added to promote rapid thermal equilibrium, the observed values were used to form a smooth table at closely spaced equal temperature intervals. This table was found to connect smoothly with that above 90 K. Deviations of observed heat capacity of the empty calorimeter from the smooth table were smaller than in the case of the calorimeter plus sample, there being none greater than 0.1 percent of net heat capacity down to 50 K, and none as large as one percent, even at the lowest temperature of measurement.

This table was converted from international to absolute joules and shifted by 0.01 K because of the newer temperature scales mentioned above. Values obtained from this table by 4-point Lagrangian interpolation were then subtracted from the observed values of C (calorimeter plus sample); the differences were converted to molar units, using a molecular weight calculated from the most recent atomic weights [8], and are listed as C_{net} in table 1. These results are plotted in figure 2, to indicate the shapes of the solid and liquid heat capacity curves. It will be noted that run 4 is missing; only fusion data were obtained from it.

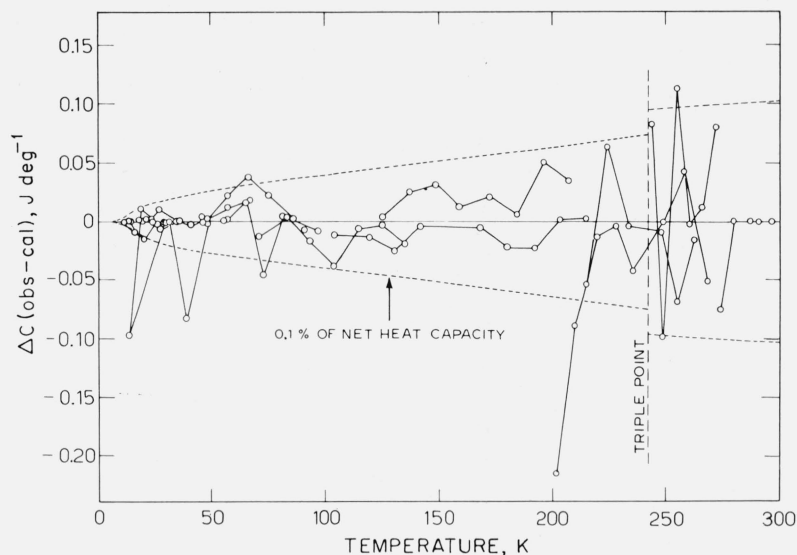


FIGURE 1. Deviations of the heat-capacity measurements on sample plus calorimeter.

TABLE 1. Observed heat capacity of bromobenzene (C_6H_5Br)

Gram molecular weight = 157.0095 g, T deg K = t deg C + 273.15

T	C_{net}	T	C_{net}	T	C_{net}	T	C_{net}
K	J K ⁻¹ mol ⁻¹	K	J K ⁻¹ mol ⁻¹	K	J K ⁻¹ mol ⁻¹	K	J K ⁻¹ mol ⁻¹
Run 1		Run 5		Run 8		Run 10	
243.310	144.489	11.279	6.318	14.141	11.167	125.358	68.957
248.692	145.007	13.502	10.251	20.305	19.159	137.083	72.778
254.565	146.293	16.675	14.590	27.342	26.563	148.248	76.466
260.388	147.061	20.430	19.307	34.177	32.109	158.975	80.001
266.166	148.081	26.643	25.932	40.340	36.140	172.173	84.543
271.897	149.201	35.557	33.097	48.172	40.410	184.101	88.747
		45.467	39.016	56.920	44.562	195.667	93.104
		55.318	43.801	65.071	48.100	206.905	97.548
Run 2		Run 6		73.107	50.902	Run 11	
104.036	61.993			81.245	54.086	202.003	95.179
118.713	66.799	30.831	29.554	90.387	57.601	209.909	98.587
130.361	70.516	38.904	35.157	45.650	39.111	219.557	102.842
141.447	74.153	47.748	40.193	56.616	44.407	228.024	106.519
168.039	83.055	56.904	44.570	66.428	48.616	235.376	109.583
180.209	87.292	66.019	48.493	Run 9		249.334	145.251
191.994	91.584	75.094	51.710	71.110	50.249	257.790	146.693
203.438	96.082	85.732	55.923	82.858	54.753	267.696	148.246
214.567	100.704	96.726	59.567	93.353	58.502		
Run 3		Run 7		103.503	61.791	Run 12	
215.147	100.869			114.578	65.493	273.951	149.301
224.101	104.942	12.548	8.707	125.042	68.846	279.454	150.413
233.548	108.861	15.682	13.266	134.546	71.882	286.737	151.824
247.755	145.001	19.933	18.690			290.496	152.614
255.219	146.104	24.284	23.540			296.358	153.891
262.629	147.428	28.981	28.019				
Note: Run 4		13.418	9.914				
consisted of fusion measurements		18.458	16.906				
		23.978	23.237				
		28.007	27.179				

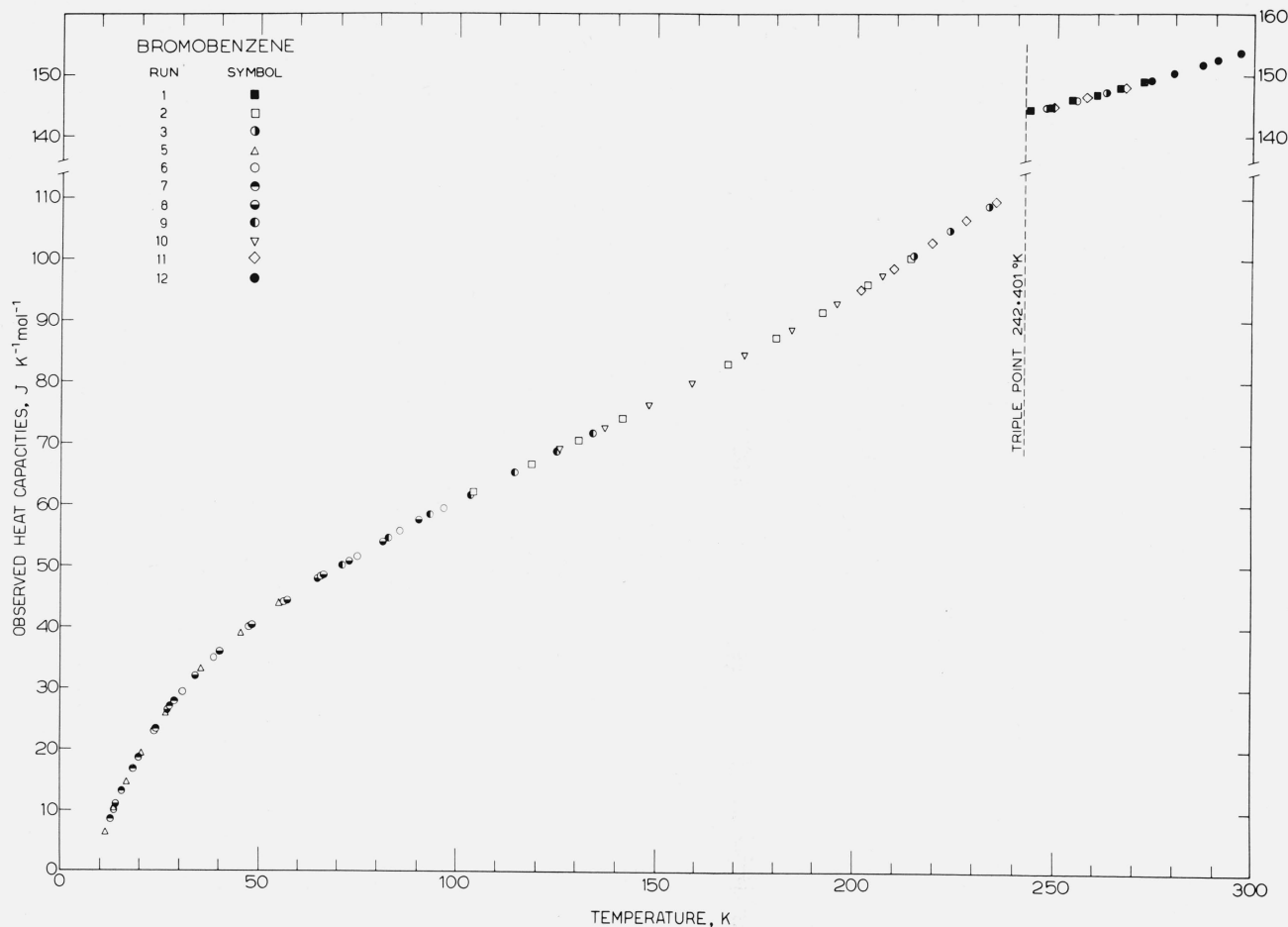


FIGURE 2. Observed values of the molal heat capacity of bromobenzene.

2.4. Triple Point and Heat of Fusion

The heat of fusion and triple point of bromobenzene, as well as the purity of the sample used, were studied experimentally in runs 3, 4, and 11. In run 11, the calorimeter and sample were heated continuously from a temperature several degrees below the triple point to a second temperature slightly above the triple point. In runs 3 and 4, heating was discontinued at several points during the melting and the equilibrium temperatures were measured. In all three cases, the heat of fusion was obtained by subtracting from the measured energy input the necessary integrals of the heat capacities of the solid and liquid (plus calorimeter), below and above the triple point. The values obtained from runs 3, 4, and 11 were respectively 10 705, 10 704, and 10 696 J mol⁻¹. Since there seems to be no bias in the results, the mean value, 10 702 ± 5 J mol⁻¹, is taken as ΔH_{fusion} for bromobenzene. Correspondingly, $\Delta S_{\text{fusion}} = 44.150 \pm 0.021$ J K⁻¹ mol⁻¹. The indicated

imprecision is twice the standard deviation of the mean.

The temperatures measured in runs 3 and 4 are plotted in figure 3 with the reciprocal of the fraction melted as abscissa. A line drawn through these points has for its temperature intercept the triple point of pure bromobenzene (242.401 K = 30.749 °C) and has a slope proportional to the mole fraction of impurity in the sample used. The proportionality constant is $-\Delta H_{\text{fusion}}/RT^2$ fusion and the calculation indicates less than 20 moles per million of soluble impurity. Such impurities would presumably include most hydrocarbon and all halo-hydrocarbon species. Other possible impurities, such as air, water, and carbon dioxide, if present in sufficient amount to affect the thermal measurements, would have been detected by transition heats during the heat capacity measurements. It seems likely that the sample used can be regarded as essentially 99.998 percent bromobenzene.

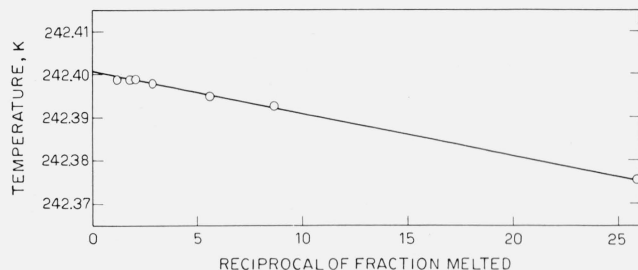


FIGURE 3. Graphical determination of triple point of bromobenzene and purity of sample.

2.5. Latent Heat of Vaporization

Since it was not feasible to modify the apparatus to operate at temperatures above ambient, and since the vapor pressures of bromobenzene up to room temperature are very low, it was decided to measure the latent heat of vaporization at only one temperature, just below that of the room. Four determinations were made, by withdrawing vapor into a cold weighing container after steady-state conditions of temperature, flow, and power input had been established. During the withdrawal of each weighed sample, constant temperature was maintained by slight adjustments of the power at measured times. It would have been desirable to make measurements at different flow rates, in order to determine the effect of any unmeasured self-cooling of the vapor. However, the low vapor pressure made it necessary to keep the calorimeter valve nearly wide open in each experiment. The data for the four determinations are given in table 2.

The discrepancies among the four values of Q/W become systematic when the values are plotted against the square of the run time, as in figure 4. The straight line which results indicates a heat loss, δQ , which is proportional to the cube of the time, since the mass of sample, W , is roughly proportional to time. The most reasonable explanation for such a heat loss is that part of the measured energy went into the formation, by conduction, of an undetected "hot spot" on a calorimeter or tube surface. This "spot" or region, δT degrees warmer than the controlled temperature of the calorimeter and the shield, then lost heat by radiation; thus, $\delta Q \propto (\delta T)^3 \propto t^3$. This explanation has been tentatively accepted as the best available for the results obtained, but it should be pointed out that no such effect was observed in a previous determination of latent heats of vaporization with the same calorimeter [2].

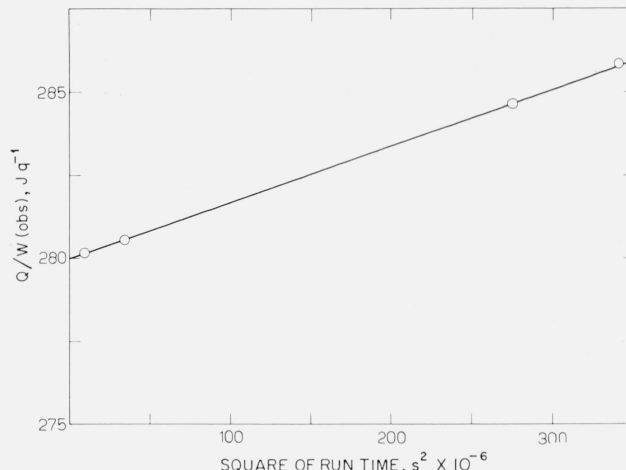


FIGURE 4. Extrapolation to zero time of the observed ratios of energy to vaporized mass, at 293 K.

The value of Q/W obtained by extrapolation to zero run time, and the resulting values of ΔH_{vap} and ΔS_{vap} at 293 K, where

$$\Delta H_{\text{vap}} = M \frac{Q}{W} \left(1 - \frac{v}{V} \right), \quad (1)$$

are given in table 2. In equation (1), v and V are the specific volumes of the saturated liquid and vapor, respectively. The expression in parentheses has the value 0.999726 in this instance, and accounts for the fact that a small amount of the vapor formed does not leave the calorimeter but replaces the vaporized liquid.

3. Thermodynamic Functions of the Solid and Liquid

The smoothed tables of heat capacity of the full and empty calorimeter at equal temperature intervals (see sec. 2.3) were subtracted; the resulting tables of heat capacity of solid and liquid bromobenzene were converted to molar units and again smoothed slightly where necessary. The table for the solid was extended to 0 K by the function

$$C = aD \left(\frac{\theta}{T} \right) \quad (2)$$

TABLE 2. Measurement of the latent heat of vaporization of bromobenzene

Run	<i>T</i> , K	<i>Q</i> , J	<i>W</i> , g	time, s	rate, g h ⁻¹	<i>Q/W</i> (293 K), J g ⁻¹
1	291.983	160.367	0.5724	3029.82	0.6801	280.17
2	293.076	228.344	.8139	5828.30	.5027	280.56
3	293.188	924.325	3.2335	18457.8	.6307	285.86
4	292.891	838.549	2.9456	16576.4	.6397	284.68
Extrapolated <i>Q/W</i>						280.0
ΔH_{vap} (293 K), J mol ⁻¹						43 963 ± 60
ΔS_{vap} (293 K), J K ⁻¹ mol ⁻¹						150.04 ± 0.2

in which $D\left(\frac{\theta}{T}\right)$ is the Debye specific heat function as tabulated by Beattie [9] and the constants $a = 37.971 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\theta = 81.184 \text{ K}$ were fitted to the lower and (12 to 20 K) of the experimental table. The resulting values for the observed heat capacity of bromobenzene, which are along the saturation curve, were converted to C_p at one atmosphere. The adjustment was found to be negligible at all temperatures for the solid. The four highest values in the table of net heat capacity for the liquid required a very small negative adjustment [10] which amounted to one part in 4000 at 300 K.

The values thus obtained for C_p of bromobenzene, plus the values at the triple point and at 0 C and 25 C

obtained by extrapolation or interpolation, form the second column of table 3. The remaining columns were calculated straightforwardly from this one, i.e.:

$$\text{Enthalpy: } H_T - H_0^c = \int_0^T C_p dT$$

$$\text{Entropy: } S_T = \int_0^T \frac{C_p}{T} dT \quad (3)$$

Gibbs free energy:

$$-(G_T - H_0^c) = \int_0^T S_T^{dT}.$$

TABLE 3. *Thermodynamic functions for bromobenzene, solid and liquid*

Gram molecular wt = 157.0095 g; $T \text{ K} = t \text{ }^\circ\text{C} + 273.15$

T	C_p	$H_T - H_0^c$	$(H_T - H_0^c)/T$	S_T	$-(G_T - H_0^c)$	$-(G_T - H_0^c)/T$
K	$J K^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J K^{-1} \text{ mol}^{-1}$	$J K^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J K^{-1} \text{ mol}^{-1}$
0	0	0	0	0	0	—
5	0.691	0.864	0.173	0.231	0.288	0.058
10	5.058	13.336	1.334	1.790	4.559	.456
15	12.253	56.312	3.755	5.183	21.415	1.428
20	18.782	134.43	6.721	9.624	58.059	2.903
25	24.295	242.51	9.700	14.425	118.11	4.725
30	28.911	375.87	12.529	19.275	202.39	6.746
35	32.735	530.28	15.151	24.029	310.73	8.878
40	35.938	702.18	17.555	28.615	442.39	11.060
45	38.753	889.03	19.757	33.013	596.54	13.256
50	41.300	1089.3	21.786	37.231	772.22	15.445
55	43.646	1301.7	23.667	41.277	968.99	17.610
60	45.936	1525.7	25.428	45.174	1184.7	19.746
65	48.045	1760.8	27.087	48.935	1420.1	21.848
70	49.876	2005.6	28.652	52.564	1673.8	23.912
75	51.630	2259.4	30.126	56.066	1945.5	25.940
80	53.555	2522.2	31.528	59.457	2234.4	27.929
85	55.629	2795.2	32.885	62.766	2539.9	29.881
90	57.485	3078.1	34.201	66.000	2861.9	31.799
95	59.027	3369.5	35.468	69.150	3199.8	33.682
100	60.659	3668.6	36.686	72.219	3553.3	35.533
105	62.351	3976.1	37.869	75.220	3921.9	37.351
110	64.010	4292.1	39.019	78.158	4305.3	39.139
115	65.639	4616.2	40.141	81.040	4703.4	40.899
120	67.244	4948.4	41.237	83.868	5115.6	42.631
125	68.841	5288.6	42.310	86.645	5541.9	44.335
130	70.442	5636.9	43.360	89.375	5982.0	46.015
135	72.060	5993.1	44.393	92.064	6435.6	47.671
140	73.696	6357.5	45.411	94.715	6902.6	49.304
145	75.346	6730.1	46.415	97.330	7382.7	50.915
150	76.998	7110.9	47.406	99.912	7875.8	52.506
155	78.651	7500.1	48.387	102.463	8381.8	54.076
160	80.323	7893.5	49.360	104.987	8900.4	55.627
165	82.025	8303.3	50.324	107.485	9431.6	57.161
170	83.751	8717.7	51.281	109.959	9975.3	58.678
175	85.497	9140.9	52.234	112.412	10532.	60.178
180	87.266	9572.8	53.182	114.845	11099.	61.663
185	89.057	10013.	54.127	117.260	11679.	63.133
190	90.888	10464.	55.070	119.659	12272.	64.589
195	92.769	10922.	56.012	122.044	12877.	66.032

TABLE 3. *Thermodynamic functions for bromobenzene, solid and liquid—Continued*Gram molecular wt = 157.0095 g; $T\text{ K} = t\text{ }^{\circ}\text{C} + 273.15$

T	C_p	$H_T - H_0^c$	$(H_T - H_0^c)/T$	S_T	$-(G_T - H_0^c)$	$-(G_T - H_0^c)/T$
K	$J\text{ K}^{-1}\text{ mol}^{-1}$	$J\text{ mol}^{-1}$	$J\text{ K}^{-1}\text{ mol}^{-1}$	$J\text{ K}^{-1}\text{ mol}^{-1}$	$J\text{ mol}^{-1}$	$J\text{ K}^{-1}\text{ mol}^{-1}$
200	94.701	11391.	56.956	124.418	13492.	67.462
205	96.696	11869.	57.901	126.781	14120.	68.880
210	98.765	12358.	58.849	129.136	14760.	70.287
215	100.90	12858.	59.802	131.485	15412.	71.683
220	103.08	13368.	60.761	133.829	16075.	73.068
225	105.24	13888.	61.725	136.170	16750.	74.445
230	107.38	14419.	62.694	138.506	17437.	75.812
235	109.51	14962.	63.668	140.838	18135.	77.170
240	111.64	15515.	64.646	143.166	18845.	78.520
242.401 (solid)	112.66	15784.	65.115	144.281	19190.	79.166
242.401 (liquid)	144.24	26486.	109.265	188.431	19190.	79.166
245	144.60	26861.	109.64	189.97	19682.	80.334
250	145.35	27586.	110.34	192.90	20639.	82.556
255	146.15	28314.	111.04	195.79	21610.	84.748
260	146.99	29048.	111.72	198.63	22597.	86.911
265	147.84	29784.	112.39	201.44	23597.	89.045
270	148.71	30526.	113.06	204.21	24611.	91.152
273.15	149.27	30996.	113.47	205.94	25257.	92.466
275	149.59	31272.	113.72	206.95	25639.	93.233
280	150.50	32022.	114.36	209.65	26681.	95.288
285	151.46	32776.	115.00	212.32	27735.	97.318
290	152.47	33537.	115.64	214.96	28804.	99.323
295	153.56	34301.	116.28	217.58	29885.	101.30
298.15	154.29	34786.	116.68	219.22	30573.	102.54
300	154.74	35072.	116.91	220.18	30980.	103.27

These integrals were found by the appropriate Debye and Einstein functions up through 16 K, and at all higher temperatures by a 4-point Simpson's rule formula applied to each temperature interval. For the purpose of integration, the intervals were two degrees up to 50 K, and five degrees from 50 to 300 K. Internal consistency was checked at each point by the identity

$$S_T = \frac{H_T - H_0^c}{T} - \frac{G_T - H_0^c}{T}.$$

In order further to promote the increasing use of the joule as the most fundamental unit of energy, it is retained in table 3 as well as elsewhere in this paper. The tabulated values may be converted to calories by dividing by 4.1840.

4. Thermodynamic Functions of the Ideal Gas

The Raman spectra of bromobenzene have been obtained by a number of investigators [11, 12, 13, 14, 15, 16, 17, 18, 19]. (Many others, not referenced here, have published spectra but have not tabulated the frequency shifts). Infrared bands have been investigated by Plum [20], by Plyler, Allen, and Tidwell [21], and by Josien and LeBas [22, 23], among others.

Assignments of the observed frequencies to the 30 fundamental vibrations (always assuming C_{2v} symmetry) have been attempted in several papers [19, 21, 23, 24]. The work by Kohlrausch and Wittek [19] was done before the fundamentals of benzene itself were well established. The assignments by LeBas [23], and by Plyler et al. [21] cover only the infrared bands. The most complete analysis appears to be that of Whiffen [24]; he also published a short table of thermodynamic functions. A review of frequency assignments for several aromatic compounds, including the monohalogenated benzenes, has been made by Wilcox, Stephenson, and Coburn [25].

By means of the usual rigid-rotator, harmonic-oscillator approximation, the thermodynamic properties of bromobenzene in the ideal-gas state were calculated. The planar C_{2v} model was assumed, in which all bond angles are 120° . The bond distances used—1.4020 Å for C-C, 1.0698 Å for C-H, and 1.8674 Å for C-Br—were those given by Rosenthal and Dailey [26] from microwave measurements. Previously reported values of the C-Br distance by Schoppe [27] and by Yuzawa and Yamaka [28] are in agreement but less precise. The product of the moments of inertia thus became $1.2533 \times 10^{-112}\text{ g}^3\text{ cm}^6$. The frequency assignment of Whiffen [24] was accepted unchanged. Although there are several discrepancies between this assignment and others, such as that of Plyler et al. [21],

the differences do not significantly affect the thermodynamic functions. The results of the calculations from 100 to 1500 K are given in table 4. Previously reported calculations, with which this table is in essential agreement, are those of Whiffen [24] and of Butler and Lielmezs [29]. Again, the tabular values may be divided by 4.1840 to obtain energy in calories.

5. Discussion of Results

When the entropy of vaporization at 293 K (table 2) is added to that of the liquid at the same temperature, from table 3, and the pressure and non-ideality corrections are applied to the sum, there is obtained the value 323.73 J K⁻¹ mol⁻¹ for the entropy of the ideal gas at one atmosphere and 293 K. (In calculating the change of entropy with pressure, a vapor pressure of 4.4 torr at 293 K was used, as obtained from Young [30]. More recent measurements, such as those of Thomas, Smith and Meatyrd [31], require a lengthy extrapolation to obtain a value at this temperature). This may be compared with the value calculated directly from statistical mechanics as it would appear in table 4, 323.63 J K⁻¹ mol⁻¹. The agreement, while to some extent fortuitous, gives added confidence in the entire set of results, and in particular lends support to the extrapolation (fig. 4) of the heat of vaporization measurements.

The heat capacities of table 3 are compared in table 5 with those reported by Stull [1]. The deviation of the earlier values from those of this research show a quite regular trend with increasing temperature, particularly in the solid region. Andrews and Haworth [32] reported heat capacity measurements on the solid at

eight temperatures from 100 to 232 K. Since the method of measurement was in principle the same as that of Stull (rate of heat transfer), it is perhaps not surprising that these measurements show a similar trend with temperature. The deviations from table 3 of the eight measurements of Andrews and Haworth range from -2.6 percent at 101.2 K to 18.4 percent at 231.7 K. Williams and Daniels [33] have measured heat capacities of liquid bromobenzene from 20 to 80 °C; their equation expressing the results gives increasingly negative deviations from the present work in the short range (273.15 to 300 K) of comparison. Other heat capacity measurements in the literature are either values at single temperatures or average values over a range of temperatures.

Stull [1] reported a triple point of 242.42 K and a heat of fusion corresponding to 10627 J mol⁻¹; the latter agrees with the present work well within the stated accuracy of Stull's measurements (3 percent). There appear to be no other direct measurements of these quantities for comparison; values of temperature and heat of melting in the presence of the atmosphere, as found referenced in handbooks, are reasonably close to the triple point and heat of fusion reported here. An experimental heat of vaporization at 298.15 K has been reported by Wadso [34]; his value of 44 540 ± 40 J mol⁻¹ is unaccountably higher than that reported here. A number of equations for the latent heats have been derived, usually based on the extensive vapor pressure data of Young [30]. The equation of Jones and Bowden [35] yields a value of Δ*H*_{vap} = 44130 J mol⁻¹ at 293 K. The agreement with the result of the present work (table 2) is quite good for a value based on vapor pressures and extrapolated below 30 °C.

TABLE 4. *Thermodynamic functions for bromobenzene, ideal gas*

Gram molecular wt = 157.0095 g, *T* deg K = *t* Deg C + 273.15

<i>T</i>	<i>C_p</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	(<i>H</i> ^o - <i>H</i> ₀ ^o)/ <i>T</i>	<i>S</i> ^o	-(<i>G</i> ^o - <i>H</i> ₀ ^o)	-(<i>G</i> ^o - <i>H</i> ₀ ^o)/ <i>T</i>
<i>K</i>	<i>J K⁻¹ mol⁻¹</i>	<i>J mol⁻¹</i>	<i>J K⁻¹ mol⁻¹</i>	<i>J K⁻¹ mol⁻¹</i>	<i>J mol⁻¹</i>	<i>J K⁻¹ mol⁻¹</i>
100	44.559	3644.0	36.440	253.59	21715	217.15
150	56.545	6166.3	41.109	273.88	34914	232.77
200	70.00	9322.8	46.614	291.95	49068	245.34
250	84.834	13190	52.760	309.15	64096	256.39
273.15	91.954	15236	55.780	316.97	71344	261.19
298.15	99.658	17631	59.136	325.36	79373	266.22
300	100.23	17816	59.388	325.97	79975	266.58
350	115.25	23206	66.303	342.56	96690	276.26
400	129.29	29324	73.311	358.88	114227	285.57
450	142.06	36114	80.253	374.86	132572	294.61
500	153.51	43508	87.017	390.43	151706	303.41
550	163.72	51444	93.535	405.55	171607	312.01
600	172.82	59862	99.770	420.19	192253	320.42
700	188.26	77944	111.35	448.03	235680	336.68
800	200.80	97417	121.77	474.02	281798	352.25
900	211.17	118032	131.15	498.29	330427	367.14
1000	219.84	139598	139.60	521.00	381403	381.40
1100	227.17	161964	147.24	542.31	434579	395.07
1200	233.39	184990	154.16	562.34	489822	408.18
1300	283.72	208600	160.46	581.24	547010	420.78
1400	243.29	232710	166.22	599.10	606036	432.88
1500	247.24	257240	171.49	616.02	666800	444.53

TABLE 5. Deviation of C_p values of Stull [1]

T	C_p (this work)	C_p (Stull)	Percent deviation ^a
K	J K ⁻¹ ·mol ⁻¹	J K ⁻¹ ·mol ⁻¹	
Solid			
90	57.485	54.89	-4.5
100	60.659	58.49	-3.6
110	64.010	61.92	-3.3
120	67.244	65.65	-2.4
130	70.442	69.54	-1.3
140	73.696	73.64	-0.1
150	76.998	77.95	1.2
160	80.323	82.01	2.1
170	83.751	86.27	3.0
180	87.266	90.71	3.9
190	90.888	95.31	4.9
200	94.701	99.75	5.3
210	98.765	104.81	6.1
220	103.08	109.96	6.7
230	107.38	115.48	7.5
240	111.64	121.17	8.5
Liquid			
250	145.35	146.36	0.7
260	146.99	150.33	2.3
270	148.71	152.97	2.9
280	150.50	154.31	2.5
290	152.47	154.89	1.6
300	154.74	155.52	0.5

$$^a \left(\frac{C_p(\text{Stull}) - C_p(\text{this work})}{C_p(\text{this work})} \right) \times 100.$$

In consideration of the precision of the experiments and the possible sources of systematic error, the accuracy of table 3 is estimated to be within ± 0.2 percent at temperatures above 50 K; the uncertainty increases at lower temperatures and may be as high as ± 2.0 percent at 15 K. A more complete picture of the thermodynamic properties of bromobenzene would be obtained if precise measurements of the heat capacity and heat of vaporization of the liquid could be continued up to at least the boiling point. Especially desirable for confirmation of the ideal-gas properties would be precise measurements of the vapor heat capacity, since the calculated heat capacity is much more sensitive than is the entropy to frequency values and anharmonicities.

Tables 3 and 4 can be extended to include the thermodynamic functions for formation of bromobenzene from the elements, by application of the heat of formation determined by Smith and Bjellerup [36].

The completion of the work and the preparation of this paper have been made possible by the fact that one of us (JFM) was assigned by the Air Force Office of Scientific Research (Office of Aerospace Research) to

the University of Rome, Italy, for an academic year. Many thanks are therefore due to the Air Force, to Professor G. Sartori for his invitation to the Istituto di Chimica Generale e Inorganica, Universita di Roma, and to the many members of the staff of that institute who have helped out with such important items as computer programming, preparation of figures, and typing.

Grateful acknowledgement is made to the many people who assisted, at various times, with the experimental measurements and calculations in the Heat Division, National Bureau of Standards. Among these may be mentioned Ruth K. Cheney, W. J. Cross, W. J. Ferguson, R. E. McCoskey, Jane W. Mellors, B. Petkof, and P. F. Wacker.

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(Paper 79A5-863)